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Gas Permeability of PVTMS/CNT Mixed Matrix Membranes

D. Bakhtin[a,*], Yu.S. Eremin[b], A.M. Grekhov[a,b], V.V. Volkov[a,b]

[a]*A.V.Topchiev Institute of Petrochemical Synthesis RAS, Leninsky prospec 29, Moscow 119991, Russia*
[b]*National Research Nuclear University MEPhI, Kashirskoye shosse 31, Moscow 115409, Russia*

Abstract

Mixed matrix membranes (MMMs) with unique transport characteristics can be prepared by the addition of the minor amounts of carbon nanotubes. Changes in the membrane performance are shown to be provided by the formation of a percolation cluster composed of nanotubes. For MMMs based on poly(trimethylvinylsilane) (PVTMS) containing carbon nanotubes (CNT), due to the formation of the CNT percolation cluster, gas permeability increases by a factor of 5-15. Numerical simulation proves that the above negative changes are provided by the agglomeration of nanotubes and subsequent deterioration of the percolation structure in the membranes.

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Keywords: mixed matrix membranes, MMM, carbon nanotubes, CNT, PVTMS, gas permeability

1. Introduction

In the recent years research is being actively carried out in the field of the development of hybrid membrane materials (mixed matrix membranes) by incorporation of these polymers with nanoparticles [1]. The interest in such polymer modification is connected with the improvement of the membrane properties: the increase in permeability coefficients, selectivity, mechanical properties, ect. [2]. These effects are connected with the change of the polymer chain mobility, the degree of crystallinity and the structure of polymer free volume which interacts with

* Corresponding author. *E-mail address:* tips@ips.ac.ru

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nanoparticles [3]. In most cases inorganic nanoparticles (TiO2, ZnO, Al2O3, SiO2, ect.), nanoporous particles with high selectivity (e.g. zeolites), nanoparticles with high aspect ratio (carbon nanotubes, carbon fibers) are used for the development of hybrid membranes [4,5]. The non-linear change of different characteristics of hybrid membranes with MCNT is described in the published works: mechanical properties, electro conductivity, magnetic properties, increase in gas and liquid permeability, etc. [6,7]. The change of permeation connected with the formation of the percolation cluster in the nanostructured domains is confirmed by the decrease of the critical concentration during the orientation of MCNT in the polymer. Nevertheless, despite the well-understood connection of the change in the permeability of the polymers and the percolation structure which is formed with the incorporation of nanoparticles, the mechanism of the selective transport in such materials is still ambiguous. In this work the research was carried out on the permeability of liquid (ethanol) and gases through the hybrid membranes based on the glassy polymer poly(vinyl thrimethylsilane) comprising MCNT (less than 3% wt.) and the critical concentration of the percolation cluster formation from the domains containing MCNT was determined.

2. Experimental

In this work, we used the multiwalled carbon nanotubes (CNT) (TAUNIT™, NanoTekhCenter LLC, Russia) prepared by chemical precipitation from a gaseous phase. According to technical specifications, TAUNIT™ carbon nanomaterial is composed of fibrils based on polycrystalline graphite with a length below 2 microns; their outer diameter varied from 20 to 70 nm, specific surface was 120-130 m2/g, and the bulk density was 0.4-0.6 g/cm3. After the treatment with nitric acid according to the standard procedure [8], density of the CNT samples was 2.26±0.03 g/cm3, specific volume was V = 0.20±0.02 cm3/g, and the surface area was S = 150±5 m2/g. The inner diameter of the nanotubes was calculated by the BJH method from the low-temperature nitrogen sorption data, and this value was 3-6 nm.

We used the commercial polymer PVTMS sample with a density of 0.86 g/cm3: the permeability coefficients were P(H2) = 220, P(O2) = 44, P(CH4) = 13 barrer [9]. Mixed matrix membranes were prepared mixing PVTMS and CNT solutions in chloroform. Carbon nanotubes were dispersed in chloroform by the ultrasound treatment for 15 min. The dimensions of agglomerates and individual CNT units were estimated by the dynamic laser scattering measurements [10]. In the experiments, we used the solutions containing 0.1 wt % of CNTs. According to the DSL method, the dimensions of agglomerates in the solution fit the dimensions of individual nanotubes with a diameter varying from 20 to 70 nm and with a length from 1 to 2 μm.

The chloroform solution of PVTMS (3 wt %) was prepared under normal conditions then and filtered. Concentrations of PVTMS and CNTs in the chloroform solutions was controoled by their optical density. The membranes were prepared by casting the PVTMS and CNT solutions onto a cellophane support. Chloroform was evaporated under normal conditions (atmospheric pressure, T = 20-24°C) until the constant weight was attained. Thickness of the prepared membranes was 25±2 μm. We prepared the PVTMS/CNT membranes containing 0.2, 0.4, 0.8, 1.2, 1.5, 2 and 3 wt % of CNTs; the error was below 0.1%. The content of CNTs in PVTMS was estimated by the helium pycnometry method (see Section 4).

The density of CNTs, PVTMS, and the related mixed matrix membranes was measured using a Micro-Ultrapyc 1200e Quantachrome density helium pycnometer; their specific surface and volume of pores were estimated by the low-temperature nitrogen sorption (Nova 1200e, Quantachrome). The inner diameter of the CNT channels d_{in} was calculated according to the BJH method [11]; the specific surface was estimated according to the BET method. Concentrations of PVTMS and CNT solutions in chloroform was controlled by their optical density using a Hach 500 DR Lange spectrophotometer; the accuracy was 0.01 abs. The integral absorption coefficient of PVTMS was measured in the 300-500 nm wavelength interval, thus making possible to control the PVTMS concentration with an accuracy of 0.2 wt %. The absorption coefficient of CNT was measured at a wavelength of 600 nm; the accuracy was not less than 0.05 wt %. The dimensions of CNTs in chloroform were studied by the dynamic laser scattering method (DLS) at a wavelength of 780 nm (Nanotrac 252, Microtrac Inc.) [17]. Permeability of ethanol through the PVTMS/CNT membranes was measured by the dynamic pressure decay method [12], the initial excessive pressure gradient was 200 atm, and the temperature was 30°C. Gas permeability of nitrogen, oxygen, methane, and propane through the PVTMS/CNT membranes were measured by the Dyness-Barrer method at a pressure gradient of 4 atm; the temperature was 19 – 24°C.

3. Results and discussion

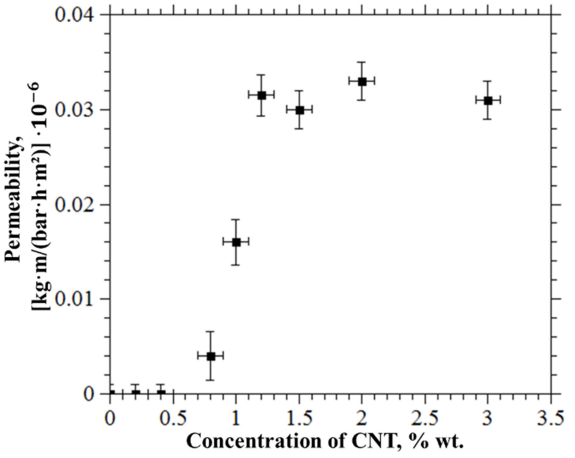

Fig. 1. Permeability coefficient of ethanol for the PVTMS/CNT membranes.

Fig. 1 presents the permeability coefficient of ethanol plotted against the CNT content in the PVTMS/CNT membranes and the plot shows three well-pronounced regions. When the CNT content in the PVTMS/CNT membranes is below 0.4 wt %, ethanol does not penetrate the mixed matrix membranes. The fact that the experimentally measured permeability of ethanol through the PVTMS-based membranes containing less than 0.4 wt % of CNT is absent means that the membrane does not have any regions which are permeable to ethanol. As the concentration of CNTs in the membrane is increased from 0.8 to 1.5 wt %, the permeability markedly increases by nearly a factor of 10. Hence, one can conclude that this increase in the ethanol permeability of the membrane takes place once a certain percolation CNT concentration is achieved and this concentration lies between 0.4 and 0.8 wt %. In this case, interconnected PVTMS/CNT regions are formed and these regions are permeable for ethanol. The number of these channels nonlinearly increases with increasing CNT concentration from 0.8 to 1.5 wt %. When the CNT content in the membrane is higher than 1.5 wt %, the growth in the membrane permeability is ceased.

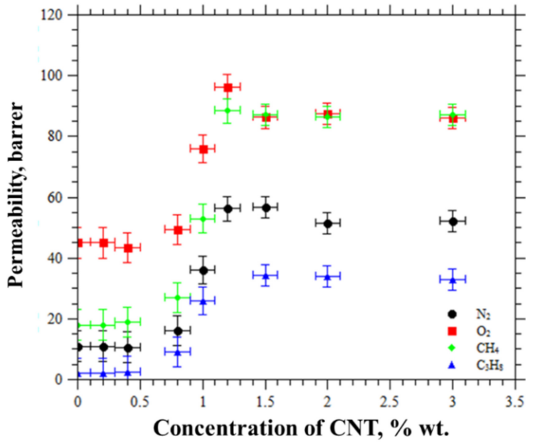

Fig. 2. Gas permeability through the mixed matrix PVTMS/CNT membranes

Fig. 2 presents the gas permeability of the mixed matrix PVTMS/CNT membranes for nitrogen, oxygen, methane, and propane plotted against the CNT concentration in the membrane, and this plot also shows three well-

pronounced concentration intervals. When the CNT content in the membrane is lower than 0.4 wt %, gas permeability of the matrix mixed membranes for all gases under study is equal to the permeability of the neat PVTMS. When the CNT content is changed from 0.8 to 1.5 wt %, gas permeability increases in the following manner: by a factor of 5 for nitrogen, by a factor of two for oxygen, 4 for methane, and 15 for propane. When the CNT content is higher than 1.5 wt %, the growth in the gas permeability is ceased and this value remains virtually constant. This increase in the gas permeability of the PVTMS/CNT membranes at the threshold CNT concentration has been reported earlier but the fact that, at the higher CNT content, the permeability becomes invariable is new [13]. This behavior was also observed for other glassy polymers. [14,15].

This nonlinear change in the permeability of the mixed matrix membranes suggests that permeability of the mixed matrix membranes is controlled by the parameters of the formed percolation cluster. Traditionally, when two different materials are mixed, any additive changes in their characteristics can be described by the mixture rule. If changes in the net membrane permeability are provided by the development of highly permeable open channels in the membrane, permeability starts to increase only when CNTs are organized into the percolation cluster; in this case, permeability should be proportional to the volume of the percolation cluster. By analogy, if permeability of the mixed matrix membranes depends on the content of nanotubes, this parameter can be described by the following relationship:

$$P_{MMM}=P_{\infty}\cdot x_{\infty}+P_{PVTMS}\cdot(1-x_{\infty}) \qquad (1)$$

where x_{∞} is the volume fraction of the membrane occupied by the percolation cluster, P_{∞} is the permeability coefficient of the percolation cluster, P_{PVTMS} is the permeability coefficient of PVTMS. Changes in the membrane permeability and x_{∞} are nonlinear when concentration of nanotubes in the membrane is above the percolation threshold [16]. At low CNT concentrations, the percolation cluster does exist or, in other words, x_{∞} is equal to zero and the presence of nanotubes has no effect on the membrane permeability. The effect of the percolation cluster on the permeability of the mixed matrix membranes was studied according to the Monte Carlo scheme which allows one to assess the conditions providing the formation of the percolation structures composed of nanotubes in the 3D space and their characteristics [16].

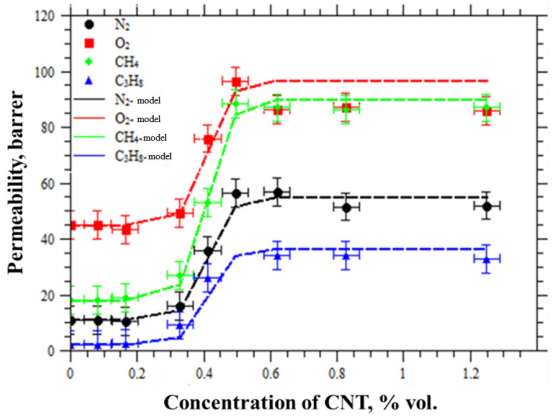

Fig.3. Gas permeability for reference (model) gases through the PVTMS/CNT membranes for (a) individual nanotubes and (b) with the account for agglomeration

Fig. 3 shows the permeability coefficients of the PVTMS/CNT membranes calculated after the substitution of x_{∞} to Eq. (1). In these calculations, we assume that there is no gas transfer through inner CNT channels, and the increase in gas permeability is solely provided by gas transport through the highly permeable layer of the modified polymer near the CNT surface. This assumption is valid only for the permeability coefficient P_{∞} but has no effect on the threshold concentrations corresponding to the formation of the percolation cluster and related changes in permeability. As follows from Fig. 3, the calculated permeability coefficients well agree with the experimental

values when the concentration of nanotubes in the matrix is below 0.5%. The development of the percolation structure and threshold changes in permeability are observed when the volume concentration of nanotubes varies from 0.3 to 0.4%. When the volume concentration of CNTs is above 0.5% (1.2wt %), the calculated permeability coefficients appear to be appreciably higher as compared with the experimental values. This disagreement can be explained by different parameters of the percolation cluster due to the agglomeration of nanotubes with increasing their content in the membrane. As follows from calculation, when the average diameter of capsules increases due to the coalescence and agglomeration of nanotubes, the volume fraction of highly permeable regions at the same concentration of the capsules in the matrix decreases. These calculations show that, when the CNT volume concentration varies from 0.5% to 1.2%, the permeability coefficient is constant only if the diameter of the capsules linearly increases from 0.05 to 0.09 units, which corresponds to the formation of the CNT agglomerates with an average size of about 100 nm.

4. Conclusions

This work shows that, for the mixed matrix CNT-containing membranes, there exists the concentration interval where gas permeability dramatically increases. At high (excessive) concentrations of CNTs, due to agglomeration of nanotubes and deterioration of the percolation structure, further increase in the CNT concentration does not provide any improvement in the membrane performance. According to the experimental results, as the CNT concentration varies from 0.4% to 1.2 wt %, permeability of the CNT-containing membranes markedly increases: 5 times for nitrogen, 2 times for oxygen, 4 times for methane, and 15 for propane. However, further increase in the CNT content does not lead to any changes in permeability.

This behavior (effect, phenomenon) was explained by the numerical simulation of a percolation cluster composed of capsules in the 3D matrix with the dimensions equivalent to nanotubes and membranes. Experimentally observed changes in the membrane permeability at high CNT concentrations can be explained with the account for the agglomeration of nanotubes (capsules) and related changes in the dimensions of the percolation cluster.

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